

DYE REMOVAL FROM SIMULATED WASTEWATER BY USING EMPTY
FRUIT BUNCH AS AN ADSORPTION AGENT

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A report submitted in partial fulfillment of the
requirements for the award of the degree of
Bachelor of Chemical Engineering

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DECEMBER 2006

ABSTRACT

The use of cheap and ecofriendly adsorbents have been studied to find an alternative substitution of activated carbon for the removal dyes from wastewater. Adsorbence from empty fruit bunches (EFB) were taken from palm oil industries were successfully remove dye from simulated wastewater. In this study, dye solution (methyl violet) were added into empty fruit bunches (EFB) which been treated with formaldehyde and sulphuric acid. This experiment's results were compared with result from similar experiment with powder activated carbon (PAC) which commonly use in industries to varying dye concentration, adsorbent dosage and pH. The result showed that the amount of the adsorbent was increased, the percentage of dye removal increased accordingly. An initial pH of the solution in the range 2-10 was favorable for the methyl violet removal for the adsorbent. The adsorption efficiency of different adsorbents was in order PAC>EFB Treated with sulphuric acid>EFB treated with formaldehyde. Adsorbents are very efficient in decolorized dilute solution. The empty fruit bunches (EFB) is a resource which has huge potential to be used for power generator. Today, it have been tried to use wastewater treatment as adsorption agent.

CHAPTER 1

INTRODUCTION

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry and agriculture. It can encompass a wide range of potential contaminants and concentrations. In the common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminant resulting from the mixing of wastewater from different resource.

A dye can generally be described as a coloured substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. In industrial wastewater, dye is the main chemical constituent of the effluent discharge from industries such as textiles, paper, plastic, cosmetic and etc. Colour in water can be harmful, carcinogenic, irritant and dangerous for the environment.

The decolourization of the textile industry wastewater is a worldwide and the use of reactive dyes turned it in a rather more serious problem. The dyes have a low fixation ratio and because they removing in wastewater treatment stations, they become a peculiar class of dyes that must be treatment before release to the environment.

Adsorption is the selective removal of a component or impurity in a fluid by contacting the fluid with a solid adsorbent, and it is widely accepted as an effective

purification method both for drinking and wastewater. The most widely use adsorbent in industries is activated carbon. However, the overlying cost activated carbon and associated problems of regeneration make more research for looking the alternative low cost adsorbents.

In Malaysia, quantity of empty fruit bunches (EFB) in the year 2003 is estimating about 26.15 million tones per year. These amounts are increase from year to year because of the expansion of matured planted area, favorable weather conditions and rainfall distribution as well as constant sunshine throughout the year. The large quantities of unused EFB have been produced by oil palm industries give serious problem for the country. With this available large resource of lignocellulose material it would be a waste to keep it underutilized. Today, many researchers try to transform EFB into more valuable substrate or products as solution to the problem.

Purpose for this thesis is to improve the empty fruit bunches (EFB) can be use as adsorbence in removing dye simulate wastewater. The result were be compared with powder activated carbon (PAC) to see the effectiveness and potential of EFB after treated with formaldehyde and acid sulphuric.

1.1 OBJECTIVES

The purpose of this study is:

- To determine the effectiveness of EFB in removing dye from simulated wastewater.
- To investigate the potential use of EFB pretreated with formaldehyde and acid sulphuric as dye removal
- To compare the result's experiment empty fruit bunches (EFB) with powder activated carbon (PAC)

1.2 SCOPE

It has four scopes for this study:

- pH values
- Adsorbence dosage
- Dye concentration
- Percentage dye removal

1.3 PROBLEM STATEMENT

Today, many industries commonly used activated carbon as adsorbent agent for dye removal. The overlying cost of activated carbon and associated problems of regeneration has force a new research in order to find other alternative low cost adsorbents agent.

Nowadays, there is numerous numbers of low cost, commercially available adsorbents which had been used for dye removal like shown in table 1.1. However, as the adsorption capacities of the above adsorbents are not very large, the new adsorbents which more economical, easily available and highly effective are still needed.

The unused empty fruit bunches (EFB) produced a large quantity by the palm oil industry. The common way to dispose the unwanted EFB is by burning in simple incinerators, burning in open, put in landfills, or left to rot in massive piles, all of which pose environmental problems. These give effect to the land space and pollution and it remains a serious problem for the country.

Table 1.1: Some Low Cost Materials for Dyes Removal from Aqueous Solution

Adsorbent(s)	Dye(s)
Bamboo dust, coconut shell, groundnut shell, rice husk	Methylene blue
Silk cotton hull, coconut tree sawdust, sago waste, maize cob	Rhodamine-B, congo red, methylene blue, methyl violet, malachite green
Parthenium Hysterophorus	Mathylene blue, malachite green
Rice husk	Malachite green
Coir pith	Acid violet, acid brilliant blue, methylene blue, Rhodamine-B
Orange peel	Acid violet 17
Indian rosewood	Malachite green
Prosopic cinetaria	Malachite green
Banana and orange peels	Methyl orange, methylene blue, Rhodamine-B, congo red, methyl violet, acid black 10B
Giant duckweed	Methylene blue

Banana pith	Congo red, Rhodamine-B, acid violet, acid brilliant blue.
Orange peel	Congo red, Rhodamine-B, procion orange
Carbonized coir pith	Acid violet, Rhodamine-B
Hardwood	Astrozone blue
Chitosan	Acid blue 25, basic blue 69
Mahogany sawdust, rice husk	Acid yellow 36
Biogas residual slurry	Congo red, Rhodmine-B, acid violet, acid brilliant blue
Plum kernels	Basic red 22, acid blue 25
Rice husk	Safranine, methylene blue

CHAPTER 2

LITERATURE REVIEW

2.1 THE DEVELOPMENT OF ADSORPTION TECHNOLOGY

The ability of some solid to remove colour from solution containing dyes has been known for over century. Similarly, air contaminated with unpleasant odours could be rendered odourless by passage of the air through a vessel containing charcoal. Although such phenomena were not well understood prior to the early twentieth century, they represent the dawning of adsorption technology which has survived as a means of purifying and separating both gases and liquids to the present day. Indeed, the subject is continually advancing as a new and improved application occurs in competition with other well-established process technologies, such as distillation and adsorption.

Attempts at understanding how solution containing dyes could be bleached, or how obnoxious smells could be removed from air streams, led to quantitative measurements of the concentration of adsorbable component gases and liquids before and after treatment with solid used for such purpose. The classical experiments of several scientist including Brunauer, Emmet and Teller, McBain, Langmuir and later by Barrer, all in the early part of the twentieth century, shed light on the manner in which solids removed contaminants from gases and liquids. As result of these important original studies, quantitative theories emerged which have withstood the test of time. It

become clear, for example, that the observed effects were best achieved with porous solids and that adsorption is the result of interactive forces of physical attraction between the surface of porous solids and component molecules being removed from the bulk phase. Thus adsorption is the accumulation of concentration at a surface.

Industrial application of adsorbents becomes more common practice following the widespread use of charcoal for decolorizing liquids and in particular, its use in gas mask during 1914-1918 World War for the protection of military personnel from poisonous gases. Adsorbents for the drying of gases and vapors included alumina, bauxite and silica gel; bone char and other carbons were used for sugar refining and the refining of some oils, fats and waxes; activated carbon were employed for the recovery of solvents, the elimination of odors and the purification of air and industrial gases; fuller's earth and magnesia were found to be active in adsorbing contaminants of petroleum fractions and oils, fats and waxes; base exchanging silicates were used for water treatment while some chars were capable of recovering metals. Finally, some activated carbons were used in medical applications to eliminate bacteria and toxins. Equipment for such tasks included both batch and continuous flow configurations, the important consideration for the design of which was to ensure adequate contact between adsorbent and fluid containing the component to be removed (the adsorbate).

2.2 ADSORPTION

Adsorption is the formation of a layer of gas, or solid on the surface of a solid. The process of adsorption involves separation of a substance from fluid phase (gas or liquid) by accumulation or concentration onto the surface of solid phase. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate.

2.2.1 MACHANISM OF ADSORPTION

Adsorption occurs in three steps. First step, the adsorbate diffuses from the major body of the stream to the external surface of the adsorbent particle. Second step, the adsorbate migrates from the relatively small area of the external surface to the pores within each adsorbent particle. The bulk of adsorption usually occurs in these pores because there is the majority of available surface area. Final step, the contaminant molecule adheres to the surface in the pores.

Adsorption at a surface is the result of binding forces between the individual atoms, ions, or molecules of an adsorbate and the surface of adsorbent. The adsorption process can be classified as physical or chemical adsorption.

They are different in:

- i. Molecules that are adsorbed by chemisorption are very difficult to remove from the adsorbent. Whereas, physically adsorbed molecules can usually be removed by either increasing the operating temperature or reducing the pressure.
- ii. Chemisorption is a highly selective process. A molecule must be capable of forming a chemical bond with the adsorbent surface for chemisorption to occur. Physical adsorption occurs under suitable conditions in most gas-solid system or liquid-solid system.

Chemisorption forms only a monolayer of adsorbate molecules on the surface and stops when all reactive sites on the adsorbent surface are reacted. Physical adsorption can form multilayer of adsorbate molecules-one stop another due to van der waals forces. The chemisorption rate increase with increasing temperature. While, the physical adsorption rate decrease with increasing temperature. The fundamental of adsorption is useful to distinguish between physical adsorption, involving only relatively weak intermolecular forces, and chemisorption which involves the formation of a chemical bond between the adsorbate molecule and the surface of the adsorbent.

Although this distinction is conceptually useful, there are many intermediate cases and it is not always possible to categorize a particular system unequivocally. However, the general features of the characteristics of physical versus chemical adsorption are presented in table 2.1.

Table 2.1: Summary of Characteristics of Chemisorption and Physical Adsorption.

Physical Adsorption	Chemisorption
i. Low heat of adsorption (<2 or >3 times latent heat of evaporation)	i. High heat of adsorption (>2 or >3 times latent heat of evaporation)
ii. Non specific	ii. Highly specific
iii. Monolayer or multilayer	iii. Monolayer only
iv. No dissociation of adsorbed species.	iv. May involve dissociation.
v. Only significant at relatively low temperatures.	v. Possible over a wide range of temperature.
vi. Rapid, non-activated, reversible.	vi. Activated, may be slow and irreversible.
vii. No electrons transfer although polarization of sorbate may occur.	vii. Electron transfer leading to bond formation between sorbate and surface.

2.3 DYES AND PIGMENTS

2.3.1 DYES

Dyes are substances that can be used to impart colour to other materials, such as textiles, foodstuffs and paper. Unlike pigments, dyes are absorbed to a certain extent by the material to which they are applied. The colours from some dyes are more stable than others. A dye that does not fade when the material it was applied to be exposed to conditions associated with its intended use is called a fast dye. Otherwise, a dye that loses its colouring during proper usage is referred to as a fugitive dye. Some of the conditions that could cause such a change in the properties of a dye include exposure to acids, sunlight or excessive heat as well as various washing and cleaning procedures. Certain dyes may be considered both fast and fugitive, depending on the material with which they are used.

The process of dyeing is carried out in a variety of ways depending on the specific dye utilized as well as the properties of the material. Silk, wool and some other textiles directly dye by simply dipping them into the colourant. Much more often, the use of a reagent known as a mordant is necessary to fix dyes to materials. A number of different compounds may be used as a mordant, but metallic hydroxides of tin, iron, chromium, or aluminum are most common. Often time, the colour that particular dyes impart is dependent on the mordant it is utilized with. Another method of dyeing involves the use of vats. For instances, the dye indigo begins as a colourless soluble substance that is dissolved in water in a vat before cloth is dipped into it. When oxygen from the air or another chemical added to the vat comes into contact with the indigo solution, an insoluble blue colour results. Batik dyeing, a process that was invented during antiquity in Java, can be used with silks or cottons and involves the application of wax to the cloth before dye treatment in order to create unusual designs and colour patterns.

A dye can generally be described as a coloured substance that has an affinity to the substrate to which it is being applied. The dye is usually used as an aqueous solution and may require a mordant to improve the fastness of the dye on the fiber.

Archaeological evidence shows that, particularly in India and the Middle East, dyeing has been carried out for over 5000 years. The dyes were obtained from animal, vegetable or mineral origin with no or very little processing. By far the greatest source of dyes has been from the plant kingdom, notably roots, berries, bark, leaves and wood, but only a few have been used on a commercial scale.

The first man made organic dye, mauveine, was discovered by William Henry Perkin in 1856. Many thousands of dyes have since been prepared and because of vastly improved properties imparted upon the dye materials quickly replaced the traditional natural dyes. Dyes are now classified according to how they are used in the dyeing process:

a) Acid Dye

Water soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers from neutral to acid dye baths. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fiber. Acid dyes are not substantive to cellulosic fibers.

b) Basic Dye

Water soluble cationic dyes that are applied to wool, silk, cotton and modified acrylic fibers. Usually acetic acid is added to the dyebath to help the take up of the dye onto the fibers. Basic dyes are also used in the colouration of paper.

c) Direct (Substantive) Dye

Dyeing is normally carried out in a neutral or slightly alkaline dyebath, at or near the boil, with the addition of either Sodium Chloride (NaCl) or Sodium Sulphate (Na_2SO_4). Direct dyes are used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.

d) Mordant Dye

As the name suggests these dyes require a mordant. This improves the fastness of the dye on the fiber such as water, light and perspiration fastness. The choice of mordant is very important as different mordants can change the final colour significantly. Most natural dyes are mordant dyes and there is therefore a large literature base describing dyeing techniques.

e) Vat Dye

These dyes are essentially insoluble in water and incapable of dyeing fibers directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye. In this liquor from these dyes have an affinity for the textile fiber. Subsequent oxidation reforms the original insoluble dye.

f) Reactive Dye

First appeared commercially in 1956 and were used to dye cellulosic fibers. The dyes contain a reactive group that, when applied to a fiber in a weakly alkaline dyebath, form a chemical bond with the fiber. Reactive dyes can also be used to dye wool and nylon in the latter case they are applied under weakly acidic conditions.

g) Disperse Dye

Originally developed for the dyeing of cellulose acetate. They are substantially water insoluble. The dyes are finely ground in the presence of a dispersing agent then sold as a paste or spray dried and sold as a powder. They can also be used to dye nylon, triacetate, polyester and acrylic fibers. In some cases a dyeing temperature of 130 degree C is required and a pressurized dyebath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fiber. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.

h) Azoic Dye

A dyeing technique in which an insoluble azoic dye is produced directly onto or within the fiber. This is achieved by treating a fiber with a diazo component and a coupling component. With suitable adjustment of dyebath conditions the two components react to produce the required insoluble azo dye. This technique of dyeing is unique in that the final color is controlled by the choice of the diazo and coupling components.

One other class which described the role dyes have rather than their mode of use is food dyes. This is a special class of dyes of very high purity. They include direct, mordant and vat dyes. Their use is strictly controlled by legislation. Many are azo dyes but anthraquinone and triphenylmethane compounds are used for colours such as green and blue. Some naturally occurring dyes are also used.

2.3.2 PIGMENTS

Pigments are the basis of all paints and have been used for millennia. They are ground coloured material. Early pigments were simply as ground earth or clay and were made into paint with spit or fat. Modern pigments are often sophisticated masterpieces of chemical engineering. In biology, pigment is any colour in plant or animal cells. Nearly all types of cells, such as skin, eyes, fur and hair contain pigment. Creatures that have deficient pigmentation are called albinos.

In the coloring of paint, ink, plastic, fabric and other material, a pigment is a dry colorant, usually an insoluble powder. There are both natural and synthetic pigments, both organic and inorganic ones. Pigments work by selectivity absorbing some parts of the visible spectrum (see light) whilst reflecting others.

A distinction is usually made between a pigment, which is insoluble and a dye which is either a liquid or is soluble. There is no well-defined dividing line between pigments and dyes, however, and some coloring agents are used as both pigments and dyes. In some cases, a pigment will be made by precipitating a soluble dye with metallic salt. The resulting pigment is called a “lake”.

Pigments are chemical compounds which reflect only certain wavelength of visible light. This makes them appear “colorful”. Flower, corals, and even animal skin contain pigments which give them their colors. More important than their reflection of light is the ability of pigments to absorb certain wavelengths.

Because they interact with light absorb only certain wavelength, pigments are useful to plants and other autotrophs-organisms which make their own food using photosynthesis. In plants, algae and cyanobacteria, pigments are the means by which the energy of sunlight is captured for photosynthesis. However, since each pigment reacts with only a narrow range of the spectrum, there is usually a need to produce several kinds of pigments, each of a different color to capture more of the sun’s energy. There are three basic classes of pigments:

a) Chlorophylls

The greenish pigments which contain a porphyrin ring. This is a stable ring shaped molecule around which electrons are free to migrate. Because the electrons move freely, the ring has the potential to gain or lose electrons easily and thus the potential to provide energized electrons to other molecules. This is the fundamental process by which chlorophyll “captures” the energy sunlight.

There are several kinds of chlorophyll, the most important being chlorophyll “a”. This is the molecule which makes photosynthesis possible by passing its energized electrons on to molecules which will manufacture sugars. All plants, algae and cyanobacteria which photosynthesize contain chlorophyll “a”. A second kind of chlorophyll is chlorophyll “b” which occurs only in “green algae” and in the plants. A third form of chlorophyll which is common is called chlorophyll “c”, and is found only in the photosynthetic members of the Chromista as well as the dinoflagellates. The difference between the chlorophylls of these major groups was one of the first clues that they were not as closely related as previously thought.

b) Carotenoids

Carotenoids are usually red, orange or yellow pigments, and include the familiar compound carotene, which gives carrots their color. These compounds are composed of two small six-carbon rings connected by a “chain” of carbon atoms. As a result, they do not dissolve in water, and must be attached to membranes within the cell. Carotenoids cannot transfer sunlight energy directly to the photosynthetic pathway, but must pass their absorbed energy to chlorophyll. For this reason, they are called accessory pigments. One very visible accessory pigment is fucoxanthin the brown pigment which colors kelps and other brown algae as well as the diatoms.

c) Phycobilins

Phycobilins are water-soluble pigments and therefore found in the cytoplasm, or in the stroma of the chloroplast. They occur only in Cyanobacteria and Rhodophyta. The vial on the left contains the bluish pigments phycocyanin, which gives the Cyanobacteria their name. The vial on the right contains the reddish pigment phycoerythrin, which gives the red algae their common name.

Phycobilins are not only useful to the organisms which use them for soaking up light energy; they have also found use as research tools. Both phycocyanin and phycoerythrin fluoresce at a particular wavelength. That is, when they are exposed to strong light, they absorb the light energy and release it by emitting light of a very narrow range of wavelengths. The light produced by this fluorescence is so distinctive and reliable, that phycobilins may be used as chemical “tags”. The pigments are chemically bonded to antibodies, which are then put into a solution of cells. When the solution is sprayed as a stream of fine droplets past a laser and computer sensor, a machine can identify whether the cells in the droplets have been “tagged” by the antibodies. This has found extensive use in cancer research, for “tagging” tumor cells.

2.4 OIL PALM EMPTY FRUIT BUNCHES (EFB)

Palm oil is very important to economy in Malaysia. It gives RM26.15 Million in 2003 of palm oil products. Malaysia is the world’s largest producer and exporter of palm oil. Currently, about 60% or 3.5 million hectares of the country’s land are under oil palm cultivation. In year 2002, 362 palm oil mills processed 60 million tonnes of fresh fruit bunch producing 11.23 millions tonnes of crude palm oil, resulting in the following solid waste residue which gives about 13.7 million tonnes of empty fruit bunch (EFB), 8.5 million tonnes of monocarp fiber, and 4.3 million tonnes palm shell.

The large quantity of EFB have been produced by oil palm industry is unused. It commonly burnt in simple incinerators, as means of disposal and the ash recycled onto

the plantation as fertilizers. This process causes air pollution and has now been banned in some countries like Malaysia. Under this route of disposal no energy is recovered. Alternatively EFB can be composted and returned to the plantation, or returned directly as mulch.

Empty fruit bunches are a good sources of organic matter and plant nutrients. It has been calculated that EFB mulching at 27 tones per hectare is equivalent to the current fertilizer practice involving inorganic fertilizers. It is claimed that using the EFB as mulch has several advantages for the nutritional sustainability of the plantation. Mulch benefits crop production because it releases nutrients slowly to the soil via microorganisms therefore effectively recycling the plant nutrients. It improves the soil structure due to better aeration, increase the water holding capacity and increase the soil Ph. It is claimed that this also increase the EFB yield over and above the increase due solely to the fertilizer value.

However, since EFB return only just over 20% efb from an average production pf 25 tonnes/EFB/Ha only 5 tonnes of EFB can be returned to the field as nutrients. So, the balance of unwanted EFB gives the big problem because lack of landfill space and recent ban on burning of solid agriculture waste in line with the Clean Air Fact. Some plantation owners claim that the benefits of EFB as fertilizer and as a soil conditioning agent are significant, while other mill owners welcome alternate methods of disposal. This is due to the inconvenience of handling and transporting, as well as the costs and [problems concerning disposal of the waste onto the plantation.

2.4.1 COMPOSITION EMPTY FRUIT BUNCHES (EFB)

Empty fruit bunchesv(EFB) as discharged from processing line contain high percentage of water (72%) and bulky in nature. It also contains some undetached fruit due to inefficient sterilization and stripping of the bunch. It is uneconomical to utilize the EFB as it is. Physical manipulation of size reduction and moisture removal is